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AGING AND DEGRADATION OF POLYOLEFINS
III. POLYETHYLENE AND ETHYLENE-PROPYLENE
COPOLYMERS

Christian Decker, et al

Stanford Research Institute

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Final Report

August 31, 1972

For the Period December 1970 to August 31, 1972

Report No. 10 for Project 8012-2

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III. Polyethylene and Ethylene-Propylene Copolymers

By: CHRISTIAN DECKER, FRANK R. MAYO, and HAROLD RICHARDSON

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This report completely replaces and then extends Report No. 9. The principal change is the insertion of a new Section 8. Further, a paragraph on the effect of oxygen pressure has been added to Section 5, and other additions have been made to the Summary and Table I.

γ -INITIATED OXIDATIONS OF POLYETHYLENE AND ETHYLENE-PROPYLENE COPOLYMERS

1. OBJECTIVE

The object of this research is to compare the effects of changes in structure and degree of crystallinity on oxidations of polyethylene (PE), ethylene-propylene copolymers (EP), and polypropylene (PP) at the same rates of γ -initiation at 45°.

2. SUMMARY

Rates of oxygen absorption and formation of oxidation products at 45° were determined in γ -initiated oxidations of thin films of low and high density PE, of atactic (APP) and isotactic (IPP) PP, and of EP copolymers. The dependence of the total oxygen absorption on rate of initiation lies between half and first order. The principal oxidation products are hydroperoxides (PO_2H), formed only by a half-order reaction, whereas dialkyl peroxides (P_2O_2) result only from a first order reaction. Carbonyl compounds ($>\text{C}=\text{O}$) are associated with reactions of both orders. These oxidation products account for 86 to 93% of the oxygen consumed; the missing oxygen is assumed to be in some alcohols (POH) and volatile products. Radiation yields (G) for O_2 absorbed and formation of PO_2H decrease sharply with increasing ethylene content of the copolymer and increasing crystallinity. In contrast, G values for formation of P_2O_2 and $>\text{C}=\text{O}$ (and thus for chain initiation) do not change much with polymer composition and crystallinity. Oxidation of IPP is somewhat slower than for APP and is accompanied by an increase in crystallinity of the sample.

The presence of dialkyl peroxide crosslinks in oxidized PE-1 was confirmed by pyrolysis of the peroxide in xylene solution (Section 8).

A few experiments with the amorphous polymers, APP and EP-A, and di-*t*-butylperoxy oxalate (DBPO) show (Section 9) that decomposition of this peroxide at 45° produced insoluble and crosslinked polymer from EP-A but not from APP, in either the presence or absence of oxygen.

However, none of the γ -irradiated films gave much insoluble polymer. Efficiencies of initiation of DBPO were much higher in EP-A than in APP, accounting partly for the difference in crosslinking. In addition, ethylene units are apparently much more easily crosslinked than propylene units. With γ -radiation, much of the expected crosslinking is offset by cleavage accompanying initiation.

3. BACKGROUND

This report is the third of four summary reports on the aging and degradation of polyolefins. The first¹ and second² deal with the aging and degradation of atactic polypropylene as initiated by DBPO¹ and by γ -radiation,² the fourth with photodecompositions of model peroxides.^{2a} This report extends our work on γ -initiated oxidations of APP to PE, IPP, and EP copolymers. Since this is the only report dealing with isotactic PP, APP and ITT are distinguished here.

In the absence of oxygen, γ -irradiation of PE leads to formation of crosslinks³ and unsaturation.⁴ Average values for these radiochemical yields are:⁵ $G_{\text{crosslinking}} = 2.0 \pm 0.4$ and $G_{(-\text{CH}=\text{CH}-)} = 1.8 \pm 0.6$, i.e., about the same values as for linear hydrocarbons such as hexadecane.^{6,7,8} The gas evolved is hydrogen ($G_{\text{H}_2} = 4.1$) with smaller amounts of methane, ethane, propane, and butane.³ Formation of alkyl and allylic radicals during γ -irradiation of PE under vacuum has been proved by electron spin resonance spectroscopy.^{9,10,11}

(1) E. Niki, C. Decker and F. R. Mayo, Peroxide-Initiated Oxidations of Atactic Polypropylene, Final Report (No. 10) for SRI Project 8012-1 (August 1972).

(2) C. Decker and F. R. Mayo, γ -Initiated Oxidations of Atactic Polypropylene, Final Report (No. 9) for Project 8012-2 (August 1972); Final Report (No. 11) for SRI Project 8012-1 (August 1972).

(2a) T. Mill, H. Richardson, and F. R. Mayo, Photodecompositions of Model Peroxides, Final Report (No. 12) for Project 8012-1 (August 1972).

(3) A. Charlesby, Proc. Roy. Soc. (London), A215, 198 (1952).

(4) M. Dole and C. D. Keeling, J. Amer. Chem. Soc., 75, 6082 (1953).

(5) A. Chapiro, Radiation Chemistry of Polymeric Systems, Interscience, New York, 1962.

It is well known that irradiation of polyethylene in the presence of oxygen leads to oxidation. The appearance of carbonyl, hydroxyl, and peroxide groups^{12,13,14} has been shown by infrared spectroscopy in thin films of PE irradiated in the presence of air. The carbonyl concentration increases linearly with the total dose, $G_{>C=O}$ being constant for films of less than 3 mils thickness.¹⁵ Chapiro¹⁶ showed that PE irradiated in air was able to initiate graft polymerization; besides dialkyl peroxide crosslinks, some hydroperoxide is also formed. Some chain peroxidation may take place in high pressure PE, involving probably the tertiary hydrogen of the branching point.¹⁷ Matsuo and Dole¹⁸ determined the total oxygen consumption and yields of carbonyl groups and of oxygenated gaseous products during γ -irradiation at 27° of high density PE in pure oxygen: $G_{O_2} = 9.9$, $G_{>C=O} = 5.0$, $G_{H_2O} = 2.5$, $G_{CO} = 1.0$, $G_{CO_2} = 0.6$. These products account for 49% of the oxygen absorbed; the rest of the oxygen uptake was assumed to be in peroxides and hydroxyl groups. At lower dose rates, these yields increase slightly, and $G_{O_2} = 12$. Using films of different thicknesses (45 μ to 1 mm), these authors also showed the importance of the rate of oxygen diffusion into the polymer. In his study of the reaction of oxygen with preirradiated PE at room temperature, Boehm¹⁹ concluded from the uv absorption curve that the initial reactions of oxygen with free allyl and dieny radicals occur about three times as frequently in the amorphous regions as in the crystalline regions.

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- (6) W. E. Falconer and R. Salovey, J. Chem. Phys., 44, 3151 (1966).
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 - (19) G. G. Boehm, J. Polym. Sci., A2, 5, 639 (1967).

In the present work, the oxygen consumption and formation of oxidation products were studied during the γ -initiated oxidations at 45° of low and high density polyethylenes, of three different ethylene-propylene copolymers, and of one isotactic polypropylene.

4. EXPERIMENTAL

4.1. Materials

The origins and properties of the polymers used in this work are shown in Table I. APP and copolymers EP-A and EP-B were purified by repeated washing of their heptane solutions with aqueous KOH and HCl solutions and repeated precipitation from methyl alcohol, but without much effect on their oxidation behavior. Because of their insolubility near ambient temperatures, the four other unstabilized polymers were used without purification.

Table I

PROPERTIES OF ETHYLENE-PROPYLENE COPOLYMERS AND POLYETHYLENE

| Polymer | Supplier | Mole Fraction of Ethylene | D_4^{20} | Fraction of Crystallinity by X-Ray | \bar{M}_n |
|---------|----------------------------|---------------------------|------------|------------------------------------|----------------------|
| APP | Avisun ¹ | 0.0 | 0.395 | 0.0 | 41,000 |
| EP-A | Enjay Polymer Laboratories | 0.37 | 0.902 | 0.00 | 110,000 |
| EP-B | Enjay Polymer Laboratories | 0.73 | 0.905 | 0.05 | 80,000 |
| EP-C | Solvay & Cie | 0.86 | 0.915 | 0.26 | |
| PE-1 | Union Carbide (DYNK) | 1.00 | 0.92 | 0.50 | >15,000 |
| PE-2 | Solvay (ELTEX) | 1.00 | 0.96 | 0.75 | 15,000 |
| IPP | Amoco Chemicals | 0.0 | 0.91 | 0.80 ^a | 102,700 ^a |

^a Crystallinity by heat of fusion; $\bar{M}_w = 427,200$; all measured on our film by Dr. J. R. Knox.

4.2. Film Preparation

Polymer films of uniform thickness (about 50 μ) were prepared by pressing polymer samples for 2 hours at 130° and 2000 psi between Teflon sheets. The press was then cooled slowly to 90° during the first hour to encourage crystallization of the material. Film densities were measured by flotation in methanol at 20-25° to compare morphological differences. The density of polyethylene in our films was only 0.5% less than before pressing.

4.3. Oxidation Procedures

Polymer films (about 400 mg) were degassed at 10^{-5} torr at room temperature during 3 hours, and a known amount of pure oxygen was then added to give a pressure of 650 torr at room temperature. Sealed tubes were then exposed to a Co γ source for 70 hours at 45°C at two dose rates, 650 or 1750 rad/min. After oxidation, the remaining gas was removed from the reaction tube previously cooled to -196° and measured with a toepler pump. Condensable products (CO₂, H₂O), removed from the reactor at room temperature, represent 6 to 10% by volume of the oxygen uptake, between 6 and 10 mole % (for all CO₂) and 3 to 5 mole % (if all H₂O), less if some water comes from the glass.

4.4. Analytical Methods

Oxidized polymer was dissolved in xylene under reflux during 3 minutes, and the solution titrated for hydroperoxide and dialkyl peroxide according to the procedure described in Section 4.1 of Ref. 2. Loss of peroxide during the 3 minutes reflux should be negligible since we found that, after 1 hour reflux, the hydroperoxide content is still 93% of the value obtained after a refluxing time of 3 minutes.

Carbonyl contents were determined directly on the oxidized film from the infrared absorptions of the band at 1720/cm. The concentration of carbonyl compounds was determined by measuring the absorbance at 5.83 μ and applying the Lambert-Beer law. The extinction coefficient was measured using 10-nonadecanone as model compound. The absorption at 3380/cm was too weak to permit determination of alcohols in the presence of hydroperoxides. ²

5. RATES AND PRODUCTS OF OXIDATION AT 45°

To assure that oxidations are not diffusion-controlled under our experimental conditions, we carried out oxidations of low density PE films of 25 to 250 μ thickness. Up to 100 μ thickness, the oxygen consumption was the same within experimental error ($\Delta O_2 = 0.092 \pm 0.002$ mole/kg PE at 1750 rad/min), whereas for 250- μ films, ΔO_2 was slightly lower (0.085 mole/kg PE). Therefore, further experiments were carried out with 50- μ films.

Oxidations of the five polyethylene and ethylene-propylene polymers were investigated at 45° after 70 hours of irradiation with total doses of 2.7 or 7.3 Mrad. Tables II and III show the oxygen uptakes and products at dose rates of 650 and 1750 rad/min, respectively. As in the oxidation of APP², PO₂H is the main oxidation product, accounting for 50 to 70% of the oxygen uptake for the copolymers and for 36 to 58% for the polyethylenes. The oxygen in P₂O₂ increases from 5 to 31% with increasing fraction of ethylene and crystallinity, and from 8 to 19% for the carbonyl compounds. These oxidation products account for 86 to 93% of the observed oxygen consumption; the missing oxygen may be POH and volatile products. Water and CO₂ (Section 4.3) account, however, for much less than the 19% of these gases reported by Matsuo and Dole.¹⁸

As in the oxidation of APP,² the dependence of the oxidation rate R_O on rate of initiation R_i lies between half and first order in accord with $R_O = aR_i + b/R_i$ or expressed in radiochemical yield, $G_O = \alpha + \beta/I^{1/2}$, where α and β apply to reactions that are first and half order, respectively, in R_i . Figure 1 compares the over-all rates for oxygen absorption and >C=O and PO₂H formation on the basis of the last equation. For all the polymers studied, the formation on P₂O₂ is independent of dose rate, and α ranges from 3.0 for PE-2 to 3.5 for APP, whereas the formation of PO₂H (Figure 1) is half order in rate of initiation ($\alpha = 0$). Figure 1 shows that the rate of formation of carbonyl compounds is first order for the polyethylenes but slightly less than first order for the copolymers. Total oxygen absorption (ΔO_2) shows both first- and half-order components. Determination of the first-order portions of these

Table II
 γ -INITIATED OXIDATIONS OF PP, PE, AND COPOLYMERS FOR 70 HOURS AT 650 RAD/MIN
 (Total dose = 2.7 Mrad; concentrations are in mole/kg polymer)

| | IPP | APP | EP-A | EP-B | EP-C | PE-1 | PE-2 |
|----------------------------------|---------------------------------------|-------------------------|------------------------|------------------------|------------------------|-------------------------|-------------------------|
| Ethylene, mole % sec H/tert H | 0 | 0 | 3.7 | 7.3 | 86 | 100 | 100 |
| Crystallinity, % | 0 | 2.0 | 4.0 | 12.8 | 26.6 | 50 | 75 |
| ΔO_2 | 0.36 | 0.44 | 0.169 | 0.074 | 0.06 | 0.045 | 0.033 |
| G | 132 | 156 | 60 | 26 | 21 | 16 | 12 |
| PO_2H | 0.30 ₁ (83.3) ^a | 0.336 (76) ^a | 0.12 (71) ^a | 0.05 (68) ^a | 0.04 (67) ^a | 0.026 (58) ^a | 0.016 (49) ^a |
| G | 111 | 119 | 42.4 | 18 | 14 | 9.2 | 5.6 |
| P_2O_2 | 0.00 ₈ (2.2) | 0.01 (2) | 0.009 (5) | 0.01 (14) | 0.009 (15) | 0.008 (19) | 0.008 (24) |
| G | 3 | 4 | 3 | 4 | 3 | 3 | 3 |
| $\angle C=O$ | 0.04 ₂ (5.8) | 0.036 (4) | 0.027 (8) | 0.017 (11) | 0.014 (12) | 0.012 (13) | 0.009 (14) |
| G | 15.3 | 12.8 | 9.5 | 6 | 5.0 | 4.2 | 3.2 |
| POH | 0.03 (4) | 0.06 (7) | 0.028 (8) | -- | -- | -- | -- |
| G | 11.6 | 21.2 | 9.9 | -- | -- | -- | -- |
| ΔO_2 acctd for, % | 96 | 89 | 93 | 93 | 94 | 90 | 87 |
| $\alpha \Delta O_2$ | 8 | 9 | 8 | 7.5 | 6.5 | 6.0 | 5.5 |
| $\beta \Delta O_2$ | 3200 | 3660 | 1300 | 480 | 370 | 250 | 170 |
| $\alpha \angle C=O$ | 5.0 | 4.6 | 4.4 | 4.2 | 4.2 | 4.0 | 3.4 |
| G_I^b | 10.6 | 11.6 | 10.8 | 11.2 | 10.6 | 10.0 | 9.0 |
| $\frac{G_{O_2} - G_I/2^c}{G_I}$ | 12 | 13 | 5.0 | 1.8 | 1.5 | 1.1 | 0.8 |

^a Numbers in parenthesis are % of ΔO_2 in indicated product.

^c Kinetic chain length in propagation.

^d 47 hours of irradiation (total dose = 1.8 Mrads).

^b $G_I = 2G_{P_2O_2} + \gamma \angle C=O$.

Table III

γ -INITIATED OXIDATIONS OF PP, PE, AND COPOLYMERS FOR 70 HOURS AT 1750 RAD/MIN
(Total dose = 7.3 Mrad; concentrations are in mole/kg polymer)

| | IPP | APP | EP-A | EP-B | EP-C | PE-1 | PE-2 |
|-------------------------------|------------------------|------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Ethylene, mole % | 0 | 0 | 37 | 73 | 86 | 100 | 100 |
| Crystallinity, % | | 0 | 0 | 5 | 26 | 50 | 75 |
| ΔO_2 | 0.65 | 0.43 ^d | 0.302 | 0.145 | 0.118 | 0.092 | 0.074 |
| G | 85 | 101 | 39.5 | 19 | 15.5 | 12.0 | 9.7 |
| PO ₂ H | 0.52 (80) ^a | 0.53 (69) ^a | 0.19 (63) ^a | 0.088 (60) ^a | 0.061 (52) ^a | 0.042 (46) ^a | 0.027 (36) ^a |
| G | 68 | 70 | 25 | 11.5 | 8.0 | 5.5 | 3.5 |
| P ₂ O ₂ | 0.023 (3.5) | 0.027 (3.5) | 0.026 (8.6) | 0.028 (19) | 0.025 (21) | 0.025 (27) | 0.023 (31) |
| G | 3 | 3.5 | 3.4 | 3.6 | 3.3 | 3.2 | 3.0 |
| >C=O | 0.09 (7) | 0.073 (4.7) | 0.057 (9.5) | 0.04 (14) | 0.036 (15) | 0.032 (17) | 0.028 (19) |
| G | 11.4 | 9.5 | 7.5 | 5.2 | 4.7 | 4.1 | 3.6 |
| POH | 0.07 (5.4) | 0.154 (10) | 0.06 (10) | -- | -- | -- | -- |
| G | 8.5 | 20 | 7.9 | -- | -- | -- | -- |
| ΔO_2 acctd for, % | 96 | 87 | 91 | 93 | 88 | 90 | 86 |
| G _I ^b | 11.0 | 11.6 | 11.2 | 11.4 | 10.8 | 10.4 | 9.4 |
| $\frac{G_{O_2}-G_I/2^c}{G_I}$ | 7.2 | 8.2 | 3.0 | 1.1 ₆ | 0.93 | 0.55 | 0.53 |

a, b, c Have the same significance as in Table II.

d 47 hours of irradiation (total dose = 4.9 Mrads).

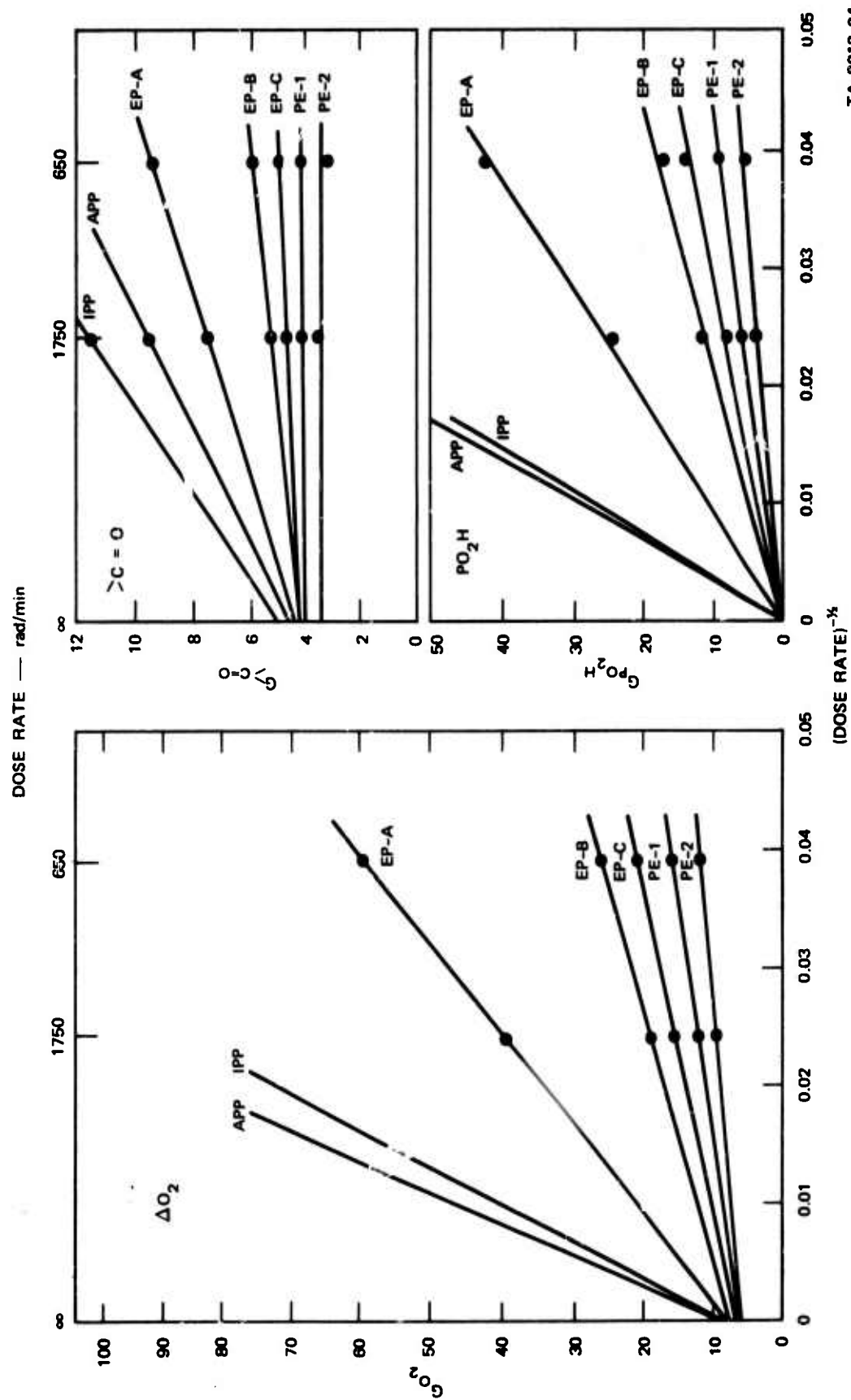


FIGURE 1 RADIOCHEMICAL YIELDS (G) AS FUNCTION OF DOSE RATES IN γ -INITIATED OXIDATIONS OF PP, PE, AND COPOLYMERS AT 45°

reactions, $\alpha_{\Delta O_2}$ and $\alpha_{>C=O}$, as in our study of PP, was assisted by extrapolation to a very high dose rate of the straight line: $G = \alpha + \beta/I^{1/2}$ (Figure 1). Values of $\alpha_{\Delta O_2}$ and $\beta_{\Delta O_2}$, reported in Table II, decrease steadily with increasing content of ethylene and crystallinity, this trend being the most marked for β .

The yield of initiating radicals G_I in each polymer was calculated by the relation $G_I = 2G_{P_2O_2} + \alpha_{>C=O}$ where $\alpha_{>C=O}$ is the intercept in Figure 1 and corresponds to the part of the carbonyl formation that is first order in R_1 . Values of G_I vary from about 9 in PE-2 to 11.6 in APP. As shown in Tables II and III, the kinetic chain length, i.e., the number of molecules of oxygen absorbed in propagation per average initiating radical $(G_{\Delta O_2} - G_I/2)/G_I$, decreases for each polymer with increasing dose rate and varies from 0.8 in high density PE to 13 in atactic PP. If, as for APP, only a small fraction of the $PO_2\cdot$ radicals formed undergo propagation out of the cage,² the true kinetic chain lengths may be 5 to 10 times higher.

The following experiment indicates that the rather high yields of P_2O_2 in our oxidations are not due to a deficiency of oxygen and the reaction of $P\cdot$ with $PO_2\cdot$ radicals. When the experiment with PE-1 in Table II was carried out with an initial 2510 instead of 650 torr of oxygen, the yields of PO_2H , P_2O_2 , and $>C=O$ were all increased slightly, to 0.31, 0.10, and 0.016 mole/kg PE, respectively. The fairly uniform increases suggest that the high oxygen pressure may have increased G for initiation by 20%. (See also Section 8).

6. EFFECTS OF POLYMER COMPOSITION

Figure 2 compares the γ -initiated oxidations of APP,² EP copolymers, and PE and shows that G_I , $G_{P_2O_2}$, and $G_{>C=O}$ do not change much with the compositions of the polymers but that G_{PO_2H} , at any dose rate, decreases markedly with increasing ethylene contents of the polymers. G_{O_2} , which approximates the sum of these quantities but depends mostly on G_{PO_2H} , is nearly as sensitive to composition. Most of the latter changes occur between APP and EP-B; in the amorphous EP-A (37% of ethylene), G_{O_2} and G_{PO_2H} are only 39% and 35%, respectively, of those for PP;

for EP-B (73% ethylene), these ratios are 18% and 16%, respectively. Consequently, the kinetic chain length for propagation (all reactions that are half order in initiator) decreases with increasing contents of ethylene (from 13 to APP to 1.8 in EPB at 650 rad/min); the ratio $k_p/(2k_t)^{1/2}$ decreases similarly. This ratio is calculated from the relation $R_o - R_i/2 = (R_i/2k_t)^{1/2}k_p[PH]$; its change with polymer composition is shown in Table IV. There is good agreement between results at different

Table IV
CALCULATION OF $k_p/(2k_t)^{1/2}$ FOR
 γ -INITIATED OXIDATIONS OF PP, PE, AND EP COPOLYMERS
(Concentrations and rates in mole/kg and hours)

| | APP | EP-A | EP-B | EP-C | PE-1 | PE-2 |
|--|------|-------------------|-------------------|-------------------|-------------------|-------------------|
| [PH] | 23.8 | 28.3 | 32.5 | 34.1 | 35.8 | 35.8 |
| Dose rate, 650 rad/min | | | | | | |
| $R_i \times 10^3$ | 0.47 | 0.43 ₇ | 0.45 ₄ | 0.43 | 0.40 ₅ | 0.36 ₅ |
| $R_o \times 10^3$ | 6.3 | 2.4 ₁ | 1.06 | 0.85 ₇ | 0.64 ₂ | 0.47 ₁ |
| $k_p/(2k_t)^{1/2} \left\{ \begin{array}{l} a \\ b \end{array} \right.$ | 1.96 | 0.62 | 0.20 ₁ | 0.15 ₁ | 0.10 ₂ | 0.07 |
| $\times 10^4$ | 4.9 | 1.55 | 0.50 ₃ | 0.38 | 0.25 ₅ | 0.17 ₅ |
| Dose rate, 1750 rad/min | | | | | | |
| $R_i \times 10^3$ | 1.27 | 1.22 | 1.24 | 1.18 | 1.14 | 1.03 |
| $R_o \times 10^3$ | 11.0 | 4.31 | 2.07 | 1.69 | 1.31 | 1.06 |
| $k_p/(2k_t)^{1/2} \left\{ \begin{array}{l} a \\ b \end{array} \right.$ | 2.04 | 0.62 ₅ | 0.21 ₂ | 0.15 ₇ | 0.10 ₃ | 0.07 ₉ |
| $\times 10^4$ | 5.1 | 1.56 | 0.53 | 0.39 ₂ | 0.25 ₈ | 0.19 ₇ |

$$^a k_p/(2k_t)^{1/2} = (\text{in } M^{-1} \text{ sec}^{-1}) = \frac{R_o - R_i/2}{R_i^{1/2} [PH]}$$

^b Corrected for 84% loss of caged PO₂· radicals.

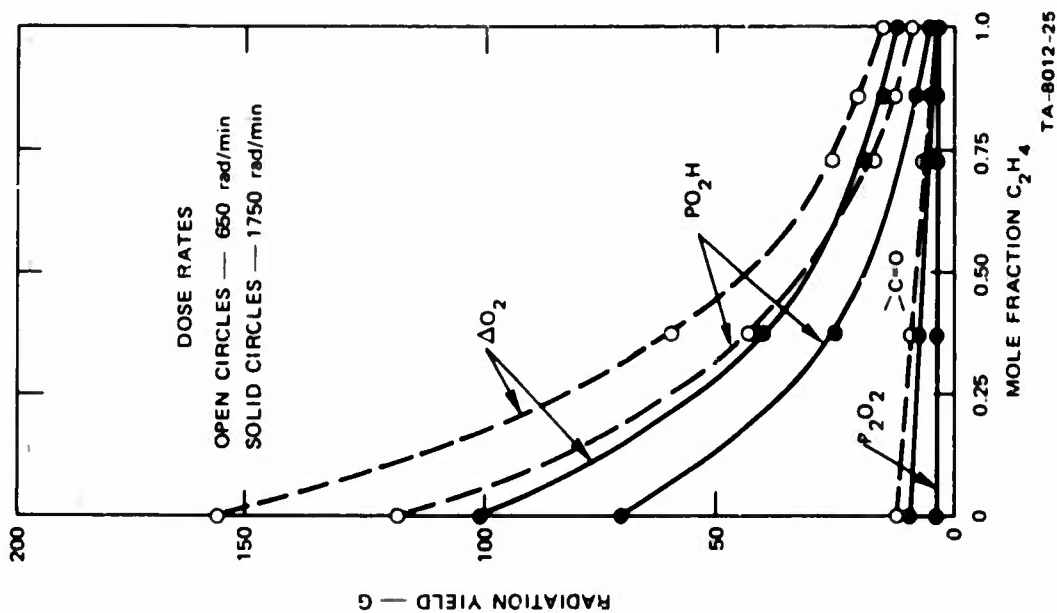


FIGURE 2 γ -INITIATED OXIDATIONS OF APP, PE, AND COPOLYMERS AT 45°

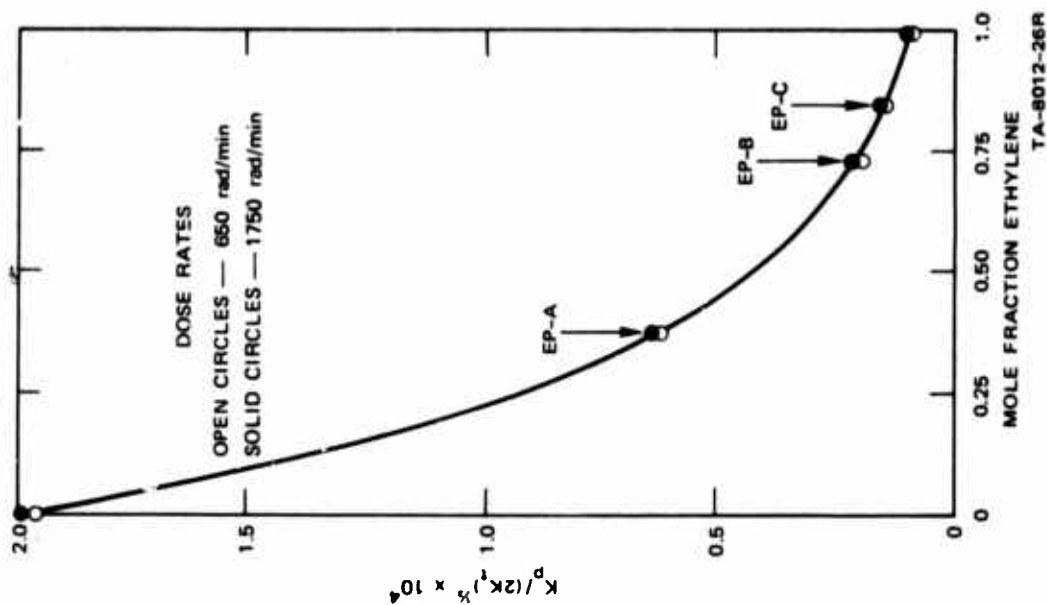


FIGURE 3 DEPENDENCE OF $k_p/(2k_t)^{1/2}$ ON ETHYLENE CONTENTS IN γ -INITIATED OXIDATIONS AT 45°

dose rates. The changes may be explained by the fact that although the propagation reaction, at least for small $\text{PO}_2\cdot$ radicals, is two to three times faster for secondary than for tertiary $\text{PO}_2\cdot$,²⁰ k_t is much higher for secondary than for tertiary peroxy radicals. Thus, the higher the fraction of ethylene in the copolymer, lower is the fraction of oxygen consumed in propagation reactions. The shape of the curve, $k_p/(2k_t)^{1/2}$ as a function of the ethylene content (Figure 3), suggests that polypropylene may be protected by increasing concentrations of ethylene. Such an observation was also made by Van Sickle,²¹ who found the copolymers to be slightly less reactive than expected on the basis of their propylene content.

7. EFFECTS OF CRYSTALLINITY

7.1. PE and EP Copolymers with High Ethylene Contents

We now compare the oxidations of the four polymers EP-B, EP-C, PE-1 and PE-2 that are 5 to 75% crystalline. Figure 4 shows how G_{O_2} and $G_{\text{PO}_2\text{H}}$ decrease sharply and almost linearly with increasing crystallinity. Our value of $G_{\text{O}_2} = 9.7$ (at 1750 rad/min) agrees with the value, 9.9, found by Matsuo and Dole¹⁸ for high density PE. The extrapolated value of G_{O_2} for a 100% crystalline polyethylene (about 6) is only one-third or one-fourth that found in the 5% crystalline copolymer. This result can be compared with the observation of Boehm,¹⁹ who deduced that the concentration of allylic $\text{PO}_2\cdot$ radicals in amorphous polyethylene was three times as high as in crystalline PE. The extrapolated values of $G_{\text{PO}_2\text{H}}$ for 100% crystalline PE are quite low, between 0.5 and 1.0. At a dose rate of 650 rad/min, the oxygen absorbed in propagation per average initiating radical decreases from 1.8 in the 5% crystalline copolymer to 0.8 in the 75% crystalline PE; the extrapolated value for 100% crystalline PE is 0.3 to 0.4 (Figure 5). The ratio $k_p/(2k_t)^{1/2}$ decreases also with increasing crystallinity to reach a very low value of about 10^{-6} in 100%

(20) B. S. Middleton and K. U. Ingold, *Can. J. Chem.*, **45**, 191 (1967); J. A. Howard, *Adv. Free Radical Chem.*, **4**, 49 (1972).

(21) D. E. Van Sickle, *J. Polym. Sci. A1*, **10**, 275 (1972)..

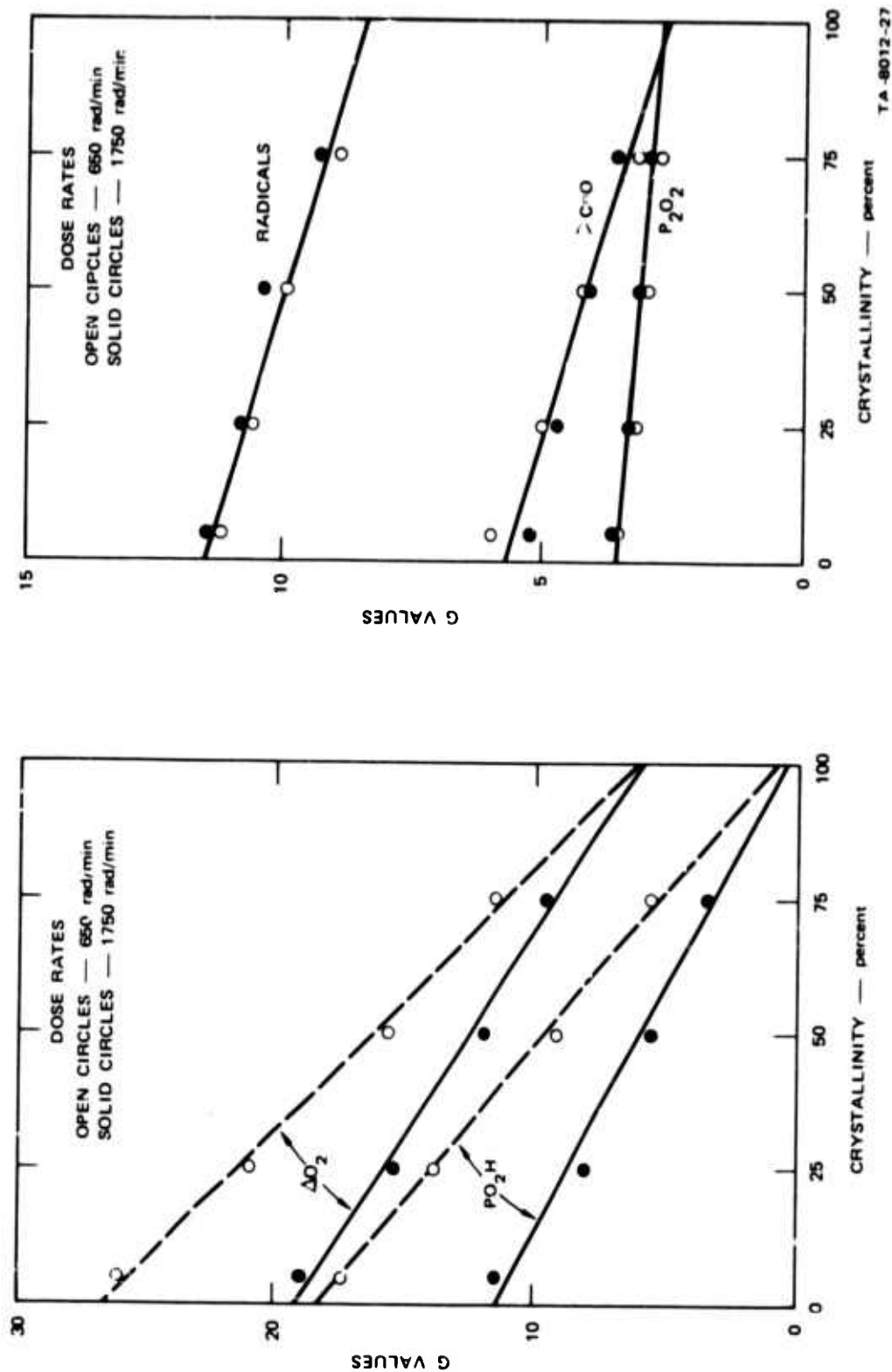


FIGURE 4 DEPENDENCE OF G VALUES FOR OXIDATION PRODUCTS ON CRYSTALLINITY

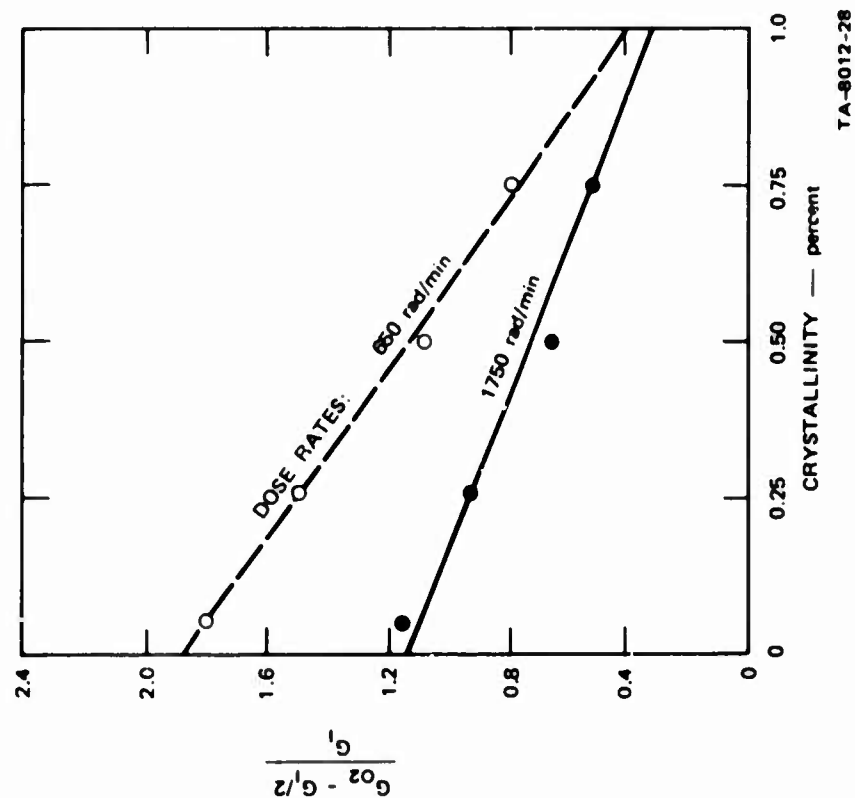


FIGURE 5 DEPENDENCE OF KINETIC CHAIN LENGTH
IN PROPAGATION ON CRYSTALLINITY OF PE

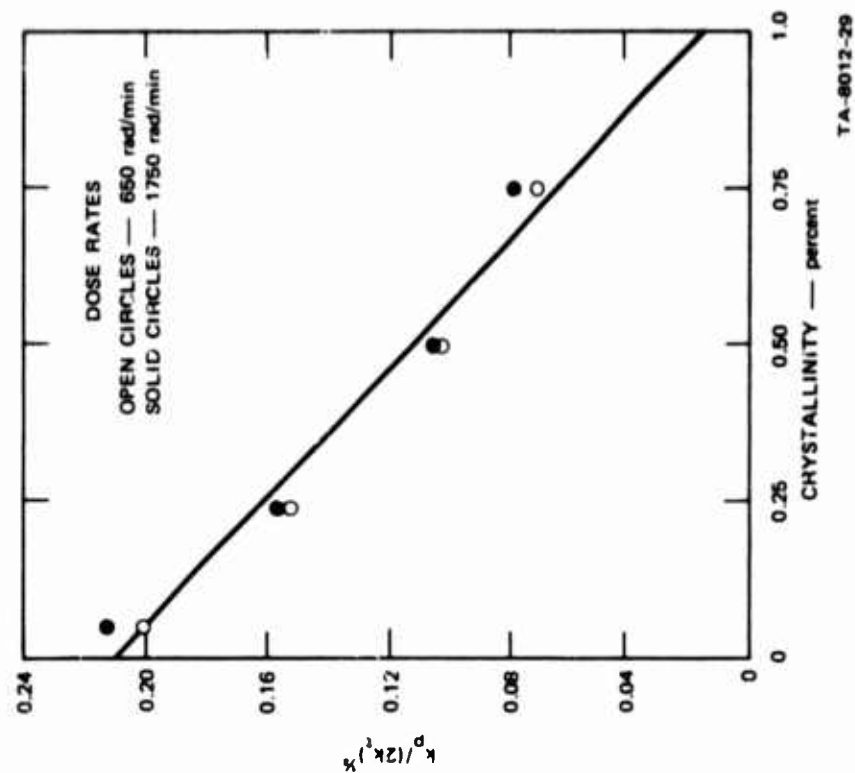


FIGURE 6 DEPENDENCE OF $k_p/(2k_1)^{1/2}$
ON CRYSTALLINITY

crystalline PE (Figure 6). Thus, most of the $\text{PO}_2\cdot$ radicals terminate by combination or disproportionation, and very few propagate in highly crystalline polyethylene. From the relative rates of oxidation, the observed propagation to give hydroperoxides takes place mostly or entirely in the amorphous regions of the four polymers considered in Figure 6.

Figure 4 shows that $G_{\text{C=O}}$ and $G_{\text{P}_2\text{O}_2}$ also decrease with increasing crystallinity, but much less than G_{O_2} or $G_{\text{PO}_2\text{H}}$. Therefore, the calculated yield of initiating radicals decreases slightly from 11.3 in 5% crystalline EP-B to an extrapolated value of about 8.5 in 100% crystalline PE. This decrease in G_I is probably due to our method for determining it (the sum of the yields of P_2O_2 and carbonyl compounds) and should reflect the fact that in crystalline regions, oxygen is less available than in the amorphous ones. Therefore, more alkyl radicals combine before adding a molecule of oxygen. However, only one of a pair of polymer radicals needs to react with oxygen to give P_2O_2 by termination.

Our calculation of G_I assumes that for each pair of initiating radicals, 1 molecule of P_2O_2 or 2 molecules of carbonyl compounds are formed. If only 1 molecule of carbonyl compound should be formed by each pair of initiating radicals, our values of G_I would be higher:

$$G_I = 2 G_{\text{P}_2\text{O}_2} + 2 \alpha_{\text{C=O}} = 14 \text{ for the 50\% crystalline PE and } 4 \text{ for the 75\% crystalline PE, instead of 10 and 9, respectively.}$$

The fraction of terminations by combination of 2 $\text{PO}_2\cdot$ radicals seems to be little affected by a change in composition and structure of the polymer. The ratio $2 G_{\text{P}_2\text{O}_2} / G_I$ (corresponding² to $b/(b + 2f)$) varies from 58% for atactic polypropylene to 63% for high density polyethylene.

7.2. Polypropylenes

To determine the effect of crystallinity on the rate of oxidation of PP, we carried out γ -initiated oxidations of isotactic PP (IPP) at 45°. Oxygen absorption and oxidation products were determined after 47 and 70 hours of γ -irradiation at dose rates of 650 to 1750 rad/min. Results are shown in Tables II and III and in Figure 7. Comparison of data for

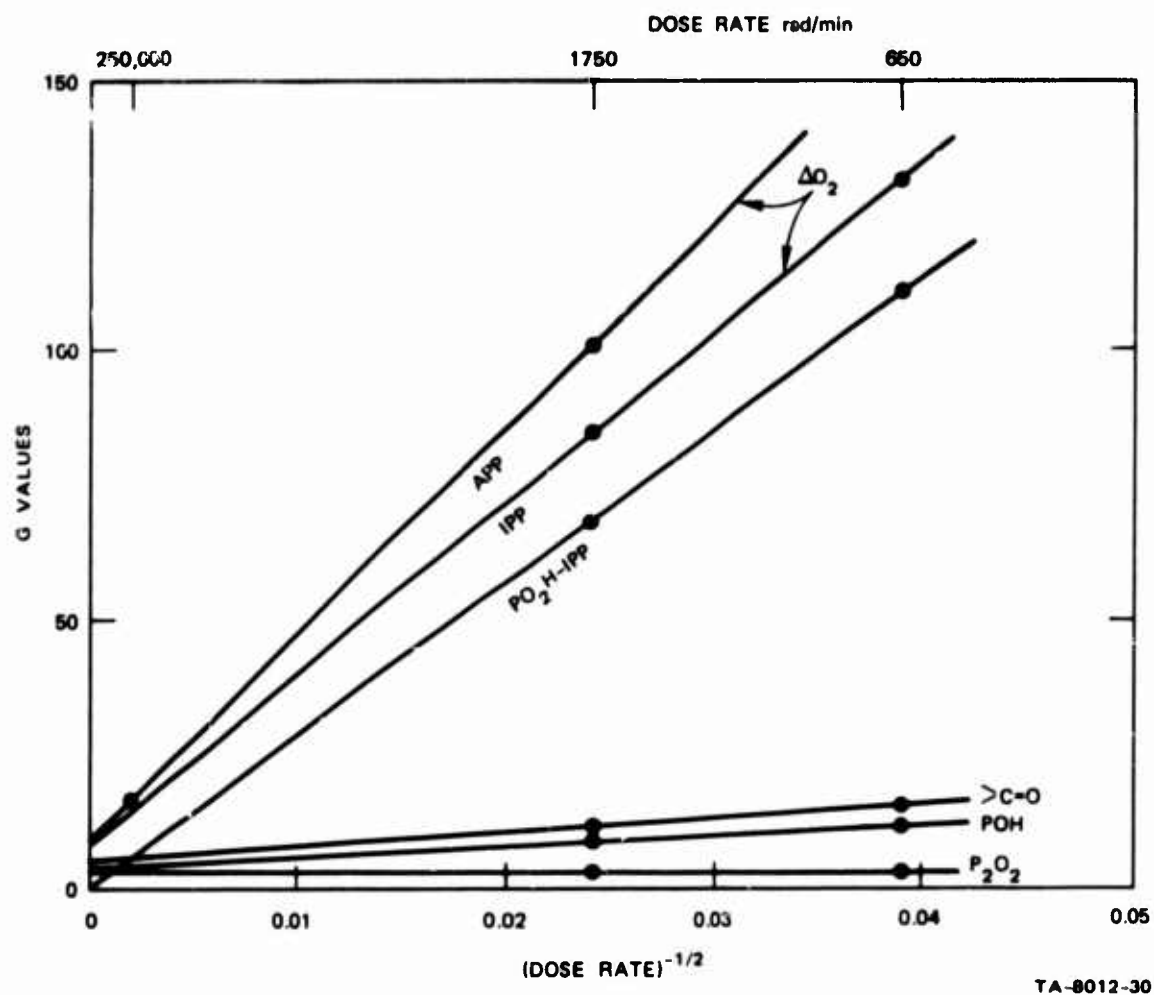


FIGURE 7 RADIOCHEMICAL YIELDS (G) AS FUNCTION OF DOSE RATES IN γ -INITIATED OXIDATIONS OF ISOTACTIC PP AT 45°

IPP and APP shows that IPP oxidizes somewhat slower than APP.² At 650 rad/min, G_{O_2} is 132 for IPP and 156 for APP. Increasing crystallinity affects PO_2H , P_2O_2 , and POH nearly proportionately, but relatively more $>C=O$ is formed in IPP. These results agree with those of Hawkins et al.,²² who found a higher R_O for APP than for IPP, and of Kato et al.,²³ who found a higher rate of formation of carbonyl compounds in photooxidation of IPP than of APP. However, in $t-Bu_2O_2$ -initiated oxidations of PP in benzene solution at 100 to 130°, Van Sickle²⁴ found that IPP oxidized 20 to 40% faster than APP.

These results, together with those of Boehm¹⁹ (who dealt with the reactions of allylic radicals with air rather than of alkyl radicals with oxygen), suggest that the overall effect of crystallinity on oxidation of PP is small but complicated. Radicals are generated by radiation, propagate, and terminate more easily in the amorphous than in the crystalline phase. However, either oxygen is able to diffuse slowly into the crystalline phase,¹⁹ or the alkyl radicals generated there can migrate into the amorphous phase. Propagation is apparently mostly intramolecular and apparently faster in the noncrystalline IPP than in the noncrystalline APP.

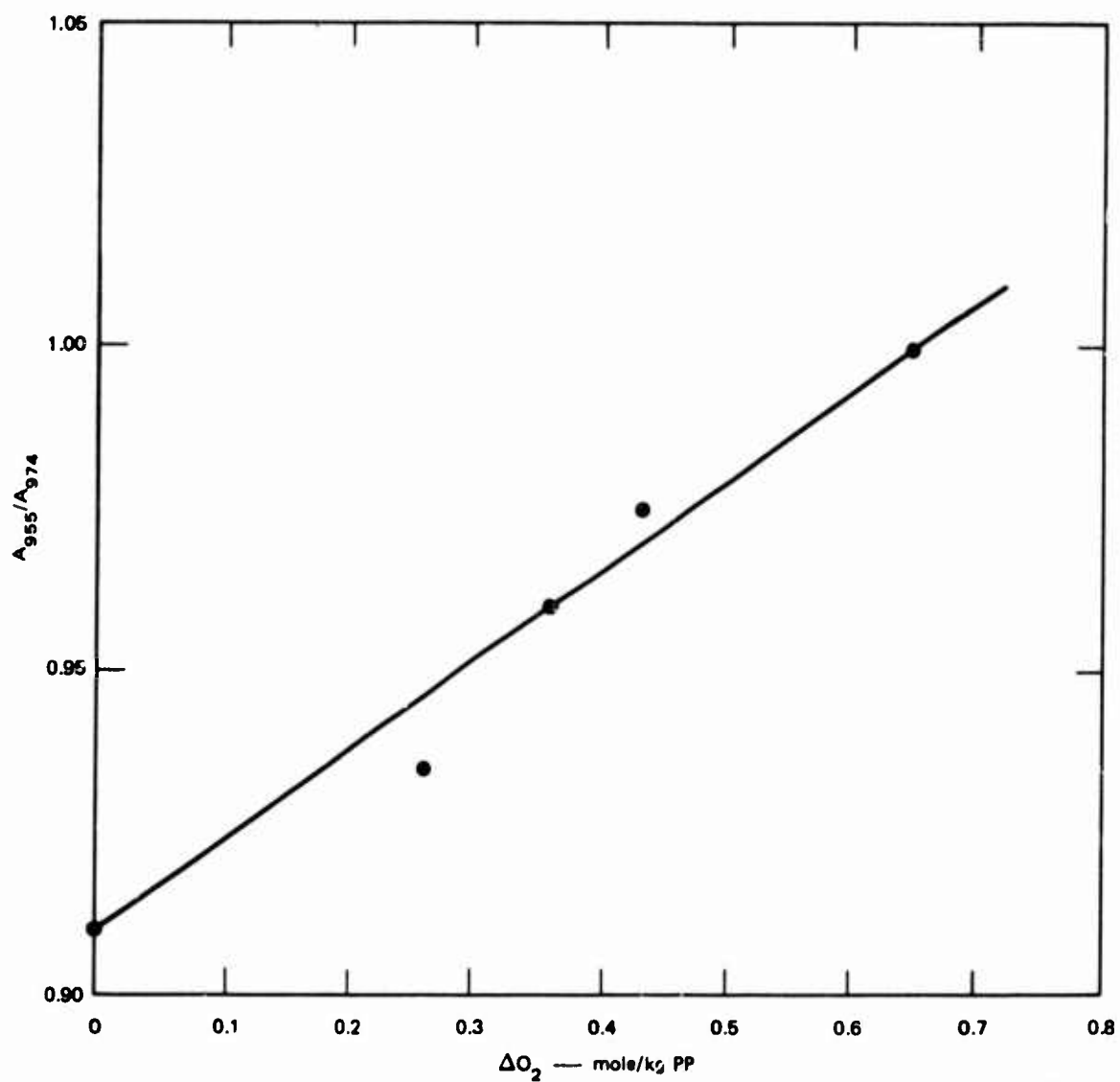
Figure 8 shows that the degree of crystallinity of IPP as measured by (absorbance at 995/cm)/(absorbance at 974/cm), increases with its degree of oxidation, as reported for PE by Winslow and coworkers,²⁵ and attributed by them to breaking and then crystallization of chains in amorphous regions.

(22) W. L. Hawkins, W. Matreyek, and F. H. Winslow, *J. Poly. Sci.*, **41**, 1 (1959).

(23) Y. Kato, D. J. Carlsson, and D. M. Wiles, *J. Appl. Polym. Sci.*, **13**, 1447 (1969).

(24) D. E. Van Sickle, *J. Polym. Sci.*, **A1**, **10**, 355 (1972).

(25) F. H. Winslow, C. J. Aloisio, W. L. Hawkins, W. Matreyek, and S. Matsuoka, *Chem. Ind.*, **1963**, 533, 1465.



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FIGURE 8 DEPENDENCE OF CRYSTALLINITY ON EXTENT OF OXIDATION (ΔO_2)
IN γ -INITIATED OXIDATIONS OF IPP AT 45°

8. FORMATION OF P_2O_2 IN OXIDATION OF PE-1

It was not expected from the work of Hiatt and co-workers^{26,27} that chain termination of two secondary alkylperoxy radicals should give more P_2O_2 than ketone plus alcohol. They found that nearly all such radical interactions in mobile solvents give alcohol, ketone, and oxygen, although they expected 3% yield of dialkyl peroxide.²⁶ However, Chapiro¹⁶ found dialkyl peroxide crosslinks in PE that had been irradiated in air, and Bakh²⁸ reported $G = 2.2$ for dialkyl peroxide formation and $G = 1.2$ for hydroperoxide formation from heptane and oxygen under the action of X rays at 25°. We have therefore confirmed such peroxide crosslinking in PE from the decrease in its molecular weight during thermal treatment. Dialkyl peroxides of PE are known to decompose at temperatures above 150° by cleavage of the O-O bond to give alkoxy radicals, which rapidly abstract hydrogen atoms from the polymer or from the solvent.²⁹ Thermolysis of preoxidized PE was therefore carried out at 200° in a xylene solution under vacuum.

A sample of PE-1 film was first oxidized at 45° by γ irradiation at 650 rad/min during 70 hours. Oxygen uptake and oxidation products formed are given in Table V. Interference from hydroperoxides was avoided by reducing them with sodium iodine using the Hiatt method).³⁰ The polymer film, free of PO_2H , was then recovered, dissolved in hot xylene, precipitated in methanol, washed several times, and finally dried under vacuum at room temperature during 24 hours. This product was then dissolved in hot xylene to give a concentration of 1.18 g/100 ml, and the

(26) R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *J. Org. Chem.*, **33**, 1428 (1968).

(27) R. Hiatt, K. C. Irwin and J. K. Castleman, *ibid.*, 1430 (1968).

(28) N. A. Bakh, Symposium on Radiation Chemistry, Academy of Sciences, U.S.S.R., Moscow, 1955, translation by Consultants Bureau, Inc., p. 119.

(29) A. Chapiro, *J. Chim. Phys.*, **52**, 246 (1955).

(30) R. Hiatt and W.M.J. Strachan, *J. Org. Chem.*, **28**, 1894 (1963).

viscosity of the filtered solution was measured at 80°. This solution was then degassed three times at 10⁻⁵ torr, sealed, and heated to 200° for 24 hours. The viscosity was then measured again. A blank experiment with unoxidized polyethylene, containing neither PO₂H nor P₂O₂, was carried out simultaneously, using all the same procedures.

The intrinsic viscosity of unoxidized PE in xylene was determined from its specific viscosities at different concentrations; $[\eta] = 0.77$. The intrinsic viscosities of the oxidized PE before and after thermal treatment were calculated from one-point measurements, using the Huggins equation: $[\eta] = [(1 + 4 k' \eta_{sp})^{1/2} - 1] / 2 k' c$, where k' was found experimentally to be 0.95. The number-average molecular weight of PE was calculated from intrinsic viscosity by the equation $[\eta] = K \bar{M}_n^a$ where $K = 13.5 \times 10^{-4}$ and $a = 0.63$.³¹

Table V shows that the molecular weight of PE increases slightly during the γ -initiated oxidation and then decreases more during thermal treatment, whereas the molecular weight of unoxidized PE decreases much less during heating at 200°. The decrease of \bar{M}_n during thermolysis of

Table V

| CHANGES IN INTRINSIC VISCOSITY OF PE DURING OXIDATION AT 45° AND PYROLYSIS OF P ₂ O ₂ IN XYLENE AT 200° | | | | |
|--|-------------------|-------------------|-------------------|-------------------|
| | Unoxidized PE | | Oxidized PE | |
| | Before Thermal | After Treatment | Before Thermal | After Treatment |
| $[\eta]$ | 0.77 ₀ | 0.76 ₀ | 0.80 ₉ | 0.74 ₃ |
| \bar{M}_n | 23,300 | 22,800 | 25,200 | 21,800 |
| Scission/kg PE | | 0.001 | | 0.007 |

(31) I. Harris, J. Polym. Sci., 8, 353 (1952).

the oxidized sample ($\bar{M}_n = 3400$) suggests that cleavage of peroxide crosslinks has occurred. The number of chain scissions produced during thermolysis was calculated to be: $\frac{25,200}{21,800} - 1 = 0.16$ scission/macromolecule or 0.007 scission/kg PE. After the value obtained with the blank (0.001 scission/kg PE) is substrated, the 0.006 scissions/kg PE corresponds to a G value of 2.1. The number of chain scissions produced by thermolysis corresponds to three-quarters of $[P_2O_2]$ as determined directly by the modified Mair and Graupner method on the oxidized PE, 0.008 mole/kg PE. The difference, if significant, could be due to some intramolecular peroxide crosslinks (peroxide rings) whose cleavage might not alter the molecular weight. After thermolysis, the \bar{M}_n of oxidized PE is lower than that of unoxidized PE, suggesting that γ rays caused some chain scissions during the oxidation (0.002 scission/kg PE). The observed increase of \bar{M}_n during the oxidation is thus the result of a peroxide crosslinking in excess of direct cleavages.

That about as many terminations occur through P_2O_2 as through disproportionation ($>C=O$) in PE (Table II and III) suggests that steric restraints on polymer radicals favor the former reaction over the latter. Although the formation of P_2O_2 might result from reaction of $P\cdot + PO_2\cdot$, this suggestion seems to be inconsistent with the absence of any marked effect of O_2 pressure on the oxidation of either PP^1 or PE (Section 5).

9. DECOMPOSITIONS OF DBPO IN EP-A

9.1. Introduction and Summary

Research on this Project 8012-2, Aging and Degradation of Polyethylene and Ethylene-Propylene Copolymers, was begun with the premise that we would have to calibrate the rate of initiation of oxidation by γ radiation against the known efficiency of initiation by DBPO, determined as with APP.¹ Considerable effort was therefore directed toward determining this efficiency of DBPO in EP-A at 45°, which requires a complete accounting for t-BuO· radicals from DBPO. Section 9.2 describes how we encountered and explained difficulties in obtaining these balances. Section 9.3 then shows that the apparently reliable efficiencies in individual experiments are erratic, unreproducible, and unsuitable for our objective, possibly because of heterogeneities in the dispersion of DBPO in EP-A. During these difficulties, unexpected progress on γ -initiated oxidations of APP showed that we did not need an independent calibration of the efficiency of this initiation, and so further work with DBPO in EP copolymers was abandoned.

The principal useful findings of the work in this section are: (1) efficiencies of initiation by DBPO in EP-A, even though erratic, are significantly higher than in APP (Section 9.3) and (2) EP-A became crosslinked and insoluble when DBPO decomposed in it, but APP did not.

9.2. Recovery of DBPO Fragments

Reports 2, 3, 5, and 7 describe our efforts to improve recoveries of t-BuO· radicals after DBPO was decomposed in bulk EP-A. Many early experiments in EP-A indicated that efficiencies of initiation and proportions of missing t-BuO groups were both unexpectedly high in comparison with APP,¹ as well as being poorly reproducible. All the products of EP-A-DBPO experiments were insoluble, and we assumed for some time, perhaps erroneously, that this new property of EP-A was responsible for our difficulties with material balances. We therefore checked our technique with soluble products of APP-DBPO reactions.

Experiment I in Table VI, with APP, offered a clue to our difficulties. This experiment was designed to test the possibility that residual pentane, used to incorporate DBPO in the polymer, was affecting bulk viscosity and therefore the product mix. A reaction vessel containing 200 mg APP¹ ($\bar{M}_n = 41,000$) dispersed on 400 mg glass wool was therefore evacuated by pumping overnight at 10^{-5} torr and 0° . The results showed nothing about residual solvent but clearly demonstrated that the DBPO could be volatilized and lost under these experimental conditions. From the CO_2 recovered on complete decomposition of DBPO, this experiment demonstrated that we could lose as much as 20% of our initial DBPO by long evacuation at 0° .

In Experiment II, the DBPO lost from the polymer was trapped in a U-tube containing toluene at liquid nitrogen temperature. After 4 hours of pumping, the DBPO in the U-tube was determined by heating the toluene solution to 60° for 4 hours and determining the CO_2 formed; it corresponded to 18.6% of the initial DBPO, which had therefore volatilized from the APP.

Experiments III, IV, and V, where DBPO was decomposed in 200 mg EP-A on 400 mg glass wool under vacuum, had nearly equal initial concentrations of DBPO. The recoveries of t-BuO fragments are only 84 to 87% on DBPO but reach 94 to 96% when based on recovered CO_2 . Experiments VI and VII with EP-A and oxygen show similar improvements in efficiency when based on CO_2 .

9.3. Comparisons of Efficiencies of Initiation

A different problem now appears. The nearly identical experiments III to V under vacuum show corrected efficiencies that range from 16 to 32%, even though differences in missing material are small. We suggest that the dispersion of DBPO in the polymer differs from experiment to experiment, possibly because part of the DBPO may have crystallized when the solvent was removed. Decomposition of crystalline DBPO may give only one product, t-Bu₂O₂, and the variations in yields of this product in Table VI, which are well beyond experimental error, may depend on the extent of this crystallization. Similar differences are seen in

Table VI

EFFICIENCIES OF RADICAL PRODUCTION BY DBPO IN APP AND EP-A^a AT 45°

| Experiment | I | II | III | IV | V | VI | VII | VIII |
|---|-------------------|--------|--------|--------|--------|----------------|----------------|----------------|
| Polymer | APP | APP | EP-A | EP-A | EP-A | EP-A | EP-A | EP-A |
| Atmosphere | O ₂ | Vacuum | Vacuum | Vacuum | Vacuum | O ₂ | O ₂ | O ₂ |
| [DBPO] ₀ , mole/kg | 0.600 | 0.541 | 0.235 | 0.205 | 0.2-9 | 0.591 | 0.616 | 0.216 |
| Products from DBPO, % of t-BuO groups. | | | | | | | | |
| t-Bu ₂ O ₂ | 72.3 | 72.2 | 64.8 | 57.6 | 53.4 | 73.8 | 72.3 | 52.2 |
| t-BuOH | 6.8 | 11.1 | 19.6 | 29.4 | 32.1 | 16.6 | 21.1 | 29.6 |
| Missing | 20.9 | 16.7 | 15.7 | 13 | 14.5 | 9.5 | 5.4 | 18.1 |
| Efficiency, % | <0 | <0 | 3.9 | 16.4 | 17.6 | 7.1 | 15.7 | 11.5 |
| CO ₂ recovery, % | 31.4 ^b | 81.4 | 89.7 | 92 | 89.4 | 93.6 | 97.4 | 91.3 |
| Products from DBPO, corrected for CO ₂ recovery ^c | | | | | | | | |
| t-Bu ₂ O ₂ | 88.9 | 80.3 | 72.2 | 62.6 | 59.7 | 78.9 | 74.4 | 57.2 |
| t-BuOH | 8.4 | 12.3 | 21.9 | 32 | 35.9 | 17.7 | 21.7 | 32.5 |
| Missing | 2.7 | 7.7 | 5.9 | 5.4 | 4.4 | 3.4 | 3.9 | 10.3 |
| Efficiency, % | 5.7 | 4.8 | 16 | 26.6 | 31.5 | 14.3 | 17.8 | 22.2 |

^aThe usual procedure was to dissolve about 0.2 g of APP ($\bar{M}_n = 41,000$) or EP-A and the required DBPO on about 0.4 g of glass wool at 0° by use of pentane as solvent. The pentane was then removed by evacuation to 10⁻⁵ mm for 2 hours at 0° before starting the experiment at 45°.

^bIn Experiment I, the evacuation was continued overnight.

^cOne t-BuO group is expected for each CO₂ found.

the oxygen experiments. We conclude that uncontrolled variables, such as nucleation and time for solvent removal, affect efficiencies of initiation but not necessarily the accuracy of the calculated numbers of polymer radicals produced. Similar aberrations may have occurred with APP,¹ but they were not serious enough to require detailed investigation.

The efficiencies of initiation by DBPO in APP average about 1% and 7% in the absence and presence of oxygen.¹ The corresponding efficiencies in EP-A in Table VI are erratic but average 25% and 18%. Although the significance of differences between the vacuum and oxygen experiments with EP-A is dubious, the efficiencies are significantly higher in EP-A than in APP. This difference suggests that separation of 2 PO₂· radicals is easier in the amorphous copolymer with 37 mole % ethylene than in APP, even though its density is slightly higher and its molecular weight is considerably higher (Table I).

10. ACKNOWLEDGEMENT

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